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Conrad P. Straub

Enviromental Health Center
Oak Ridge, Tennessee

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SOME OBSERVATIONS ON THE REMOVAL OF RADIOACTIVE MATERIALS FROM WASTE SOLUTIONS

Conrad P. Straub*

*Sanitary Engineer, Public Health Service, ~~on loan~~, Oak Ridge National Laboratory, Oak Ridge, Tennessee.

Environmental Health Center assigned to

At Oak Ridge National Laboratory the responsibility for liquid radioactive waste disposal has been delegated to two divisions of the Laboratory: the Chemical Technology Division and the Health Physics Division - the latter through its Radioactive Waste Disposal Research and Development Section. The Chemical Technology Division is responsible for the control of the wastes at their source, and for the treatment of wastes resulting from chemical processing and from the separation of reactor-produced radioactive isotopes. Thus, it is concerned primarily with the treatment of relatively small volumes of concentrated and highly radioactive materials. To the Radioactive Waste Disposal Research and Development Section is assigned the responsibility of developing techniques for treating the residual radioactive wastes. Before discharge into waters beyond the controlled area of operation is permitted, the wastes must meet limits of radioactive concentration prescribed by the Health Physics Division. For example, the maximum permissible tolerance concentration of mixed fission products in water has been set at 10^{-7} microcuries per cubic centimeter. Limits have been established also for other radioactive isotopes.

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Since sanitary engineers and sanitary chemists have been engaged and are engaged in the treatment of large volumes of domestic and industrial wastes containing low concentrations of foreign matter, the Radioactive Waste Disposal Research and Development Section is following the sanitary engineering approach in developing techniques for the treatment of the residual radioactive wastes.

An element is radioactive when its nuclei are unstable, and when unstable gives off radiations in the form of alpha and beta particles or gamma rays. It makes little difference chemically whether one deals with the radioactive or stable form of a particular chemical element. In organic and inorganic chemistry, however, the reactions usually involve macro quantities of the reacting substances, but in radiochemistry micro or tracer quantities are encountered more frequently. As a result of this the radiochemical reaction may not always follow the known stoichiometric reaction, and difficulties sometimes may arise. However, in the examples given later, it will be noted that the techniques that apply to the treatment of chemical wastes may apply to the treatment of radioactive chemical wastes.

Sources and Nature of Wastes

In a recent release[1*] the U.S. Atomic Energy Commission states that there are two major sources of radioactive waste:

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*Numbers refer to bibliography.

"1. The production phases of the national atomic energy program - the huge separation plants and the nuclear reactors.

"2. The laboratories and hospitals where radioactive materials are used for research tools for medical treatment".

In the explosion of an atomic bomb radioactive products may be released which may produce additional radioactive wastes.

Nuclear Reactors and Separation Plants. Before uranium or other fissionable ores are ready for exposure to neutron bombardment in the pile the materials must be processed. It is only after they are subjected to neutron bombardment that the highly radioactive materials are produced. Each atom which undergoes fission normally produces two fission products. Experiments show that the process is asymetric and produces fission products that can be classed as a light and a heavy group[2]. Usually included in the light group are elements of atomic number 36 through 44, and in the heavy group elements of atomic number 52 through 61. Many of these are fairly long-lived and are listed in Table 1. Fission product yields for U^{233}, U^{235}, and Pu^{239} have been published[2].

Chemical processing is necessary to separate the more valuable fission products for isotopic use in medicine and industry. To reduce the activity by natural decay the remaining substances are discharged to waste tanks where they are stored. If it can be done economically, storage

is desirable to eliminate the discharge of those radioisotopes for which uses have not been found as yet, but for which future research may find use.

Where large volumes of water are required for cooling the pile, as at Hanford, Washington, disposal of the radioactive cooling water is a problem. To minimize the amount of induced radioactivity the cooling waters are pretreated for the removal of such elements as iron, chlorine, calcium, and sulfur.

Isotope Usage. During the past few years isotopes have found wide use in the medical and industrial fields. The extent of this use may be illustrated by data, which are shown in Figure 1, giving the number of monthly shipments from the Isotopes Division, Oak Ridge National Laboratory. Since the first shipments in August, 1946, the increase has been continuous and rapid. It will be seen that the present rate of shipments is of the order of 700 per month, and by the end of July, 1950, a total of 16,030 shipments (project, non-project, and foreign) had been made. The isotopes most frequently shipped and which accounted for approximately 75 per cent of the total shipments were P^{32}, I^{131}, C^{14}, and Na^{24}.

In general, small amounts (microcurie and millicurie quantities) of radioactive materials are used in tracer experiments and the wastes which result from their discharge are ~~low~~ small in volume and low in activity. Larger

quantities (both in volume and in activity) may be discharged from hospitals where isotopes are finding widespread use as therapeutic agents.

Atomic Bomb Explosion. In addition to the radioactivity released in the explosion of an atom bomb, the neutrons discharged will produce activity in other substances. This activity, called induced activity, will be quite variable depending primarily upon the elements in the vicinity of the explosion and the type of blast (air, subsurface, or water). Radioactive wastes may result from the direct deposition of radioactive particles into water courses or from the flow of wastes produced in the decontamination of buildings, equipment, etc. where water is used as the decontaminating agent. Except that there may be a greater variety of radioactive materials, the techniques which may be applied to the treatment of these wastes will be similar to those proposed for treating radioactive wastes from other sources. It is not believed that these wastes will constitute too serious a hazard, inasmuch as water treatment techniques (coagulation, filtration, softening, etc.), if available, will certainly decrease the amount of activity in any waters used for potable or industrial purposes.

Removal of Radioactivity

Control [redacted] at their source is just as improtant in the treatment and disposal of radioactive wastes as in the treatment and disposal of domestic and industrial wastes. Until more is learned of what

occurs, the discharge of radioactive materials into streams should be considered as a last resort and should be looked on with great disfavor. Little information is available concerning the processes involved in the concentration of ~~activity~~ radioactive substances by specific muds and soils, by benthos in the stream, by plankton and by other flora and fauna which may spend part or all of their life cycle in the receiving stream. As shown by Ruchhoft[3], heavy concentrations of plutonium are adsorbed by activated sludge. Considerable unpublished data are available which indicate that muds, clays, activated carbons, etc., have an affinity for adsorbing certain radioactive materials.

complete the thought

Of the methods known to sanitary engineers and chemists for treating domestic and industrial wastes, the following have been suggested as possible modes of attack in solving problems incident to the treatment and disposal of radioactive wastes: evaporation, carrier precipitation (coagulation), sand filtration, ion-exchange (natural clays and synthetic resins), electrodialysis, metallic displacement or scrubbing, differential volatility, electrolytic separation, solvent extraction, biological processes, and crystallization. These specific treatment methods as they apply to the removal of radioactive materials will be noted below.

Evaporation. For the concentration of large volumes of wastes containing small amounts of radioactive materials, evaporation, although expensive, will remove practically all of the activity from the liquid fraction and will concentrate that activity in the solid residue or

slurry. It is reported[4] that a decontamination factor of at least 100,000 is possible by this method. To permit disposal as a solid and as a means of reducing the amount of space required for storage of radioactive materials, evaporation is desirable.

If the reader knows these chemical symbols he does not need to be told that high pH is very alkaline

Carrier Precipitation. Carrier precipitation or coagulation is used extensively in the treatment of many industrial wastes, and has been adapted to the removal of certain radioactive materials. For the removal of As, Sb, Mo, Se, Te, and Ce, coagulation has been applied with varying success; however, with Ru, Cs and Pu removals were very satisfactory. In many instances coagulation was most effective at high pH values (very alkaline). Studies have been made at the Oak Ridge National Laboratory in which routine and special coagulation techniques were applied to the removal of specific isotopes from water solutions to which radioactive chemicals had been added. Using routine alum and lime coagulation Placak and Lyle[5] obtained removals of specific isotopes as shown in Table 2. Since a study indicated that there appeared to be more insoluble phosphates than hydroxides, Lauderdale[6] carried out experiments in which he employed a modified phosphate coagulation technique. The studies were carried out at a pH of about 11.5 using up to 200 ppm Na_3PO_4 or KH_2PO_4 and lime. Some typical results are indicated in Table 3. Using pilot plant equipment having a capacity of approximately 1000 liters per day the writer[7] studied the removal of P^{32} and I^{131} by conventional water treatment units (coagulation, settling, and filtration).

Removals are indicated in Table 4. At the Massachusetts Institute of Technology similar results were obtained for the removal of P^{32} by conventional water treatment units.

Sand Filtration. Although little information is available on the removal of ~~radioactivity~~ radioactive substances by sand filtration, unpublished communications indicate that ~~radioactivity~~ many of them may be removed by adsorption on sand grains. In the filtration of P^{32} and I^{131} our experience showed that the former was removed by filtration as shown in Table 5, but that there was no measurable removal of the latter.

Ion-Exchange. With the newer high capacity cationic and anionic synthetic resins many radioactive elements may be removed from large volumes of dilute wastes. Unpublished information[8] indicates that Na, Ba, and La are removed in cationic resin columns, and that Te and Mo are removed in anionic resin columns. The work of others indicates that under suitable conditions Sr, Cs, Ce and the rare earths may be removed by cation exchangers . It is believed that ion-exchange columns may have a very definite use as polishing units following the removal of gross radioactive contaminants by coagulation or carrier precipitation and filtration in the conventional water treatment-type units.

Natural soils and clays are known to take up ~~radioactivity~~ radioactive elements by adsorption. For the removal of radioisotopes from a mixed fission

waste, Lauderdale[6] used local kaolinitic and montmorillanitic clays as adsorbing agents. Although the dosages of clay required were very large, to 50,000 ppm, removals of 80 to 85 per cent were obtained. Other soils have been shown to adsorb Pu, Sr, Y, Ce and Pr. As mentioned earlier P^{32} was taken up during filtration in a conventional-type water treatment plant. Acid and alkali washes were found effective for eluting the adsorbed substances.

Metallic Displacement or Scrubbing. This technique has been applied successfully to the recovery of Ru and other substances.

Electrodialysis, Electrical Separation, and Differential Volatility. As they apply to the treatment of radioactive wastes no applications of these techniques are known to the writer.

Biological Processes. By extraction and concentration on aerated activated sludges, Ruchhoft[3] was able to demonstrate reductions of about 96 per cent in the alpha activity of Pu as a result of single-stage treatment. Somewhat similar results have been obtained in preliminary studies by the writer[7] in the removal of I^{131} by aerated and stirred activated sludges. Reid, at Johns Hopkins University, has studied the accumulation of I^{131} by slimes found in sewers.

If the radioactive materials are long-lived and are retained on the sludge throughout the sludge treatment period, their accumulation may pose a serious hazard. Dried digested sludges, which are used as

fertilizers, are spread frequently on park and golf course lawns, and as a result, hazardous concentrations of radioactive materials may occur.

Crystallization. Cook and Wilkinson[9] report that it may be possible to freeze out a large fraction of the water leaving the radioactive materials in concentrated solution, but that this method had never been investigated. The writer[7] has made some preliminary study in which very small samples (volumes to 200 ml) were used and has found that concentration ~~of the radioactivity~~ does ~~not~~ take place. Concentration factors approaching 10^2 were obtained. Additional equipment has been procured for study of samples of much greater volume. Crystallization is not restricted to separation of solids by freezing alone, but may be applied to many forms of chemical reactions.

Conclusions

Many of the methods available for use in the treatment of industrial wastes may be utilized in the treatment of radioactive wastes; however, it must be remembered that, just as in sewage and industrial waste treatment, separation of the wastes into ~~its~~ liquid and solid fraction and discharge of the ~~liquid~~ fraction does not solve the problem. The ~~sludge or solid~~ residue remains for disposal. All that can be accomplished is to concentrate the radioactive fraction into a smaller volume to permit disposal either as a sludge or slurry ~~or it may be possible to dewater the material further and dry it~~. Where incineration

is possible, providing precautions are taken to prevent contamination by volatile gases or fly ash, further concentration or reduction in volume may be obtained. Care must be given also to the removal of the resultant ash. The reduced volume of solid material then may be placed in suitable containers and buried or stored in controlled areas for further utilization or recovery.

buried in controlled area or stored for decay or future recovery.

Bibliography

1. United States Atomic Energy Commission. Handling Radioactive Wastes in the Atomic Energy Program. U.S. Government Printing Office, Washington, D.C. October, 1949.

2. Lapp, R.E. and Andrews, H.L. Nuclear Radiation Physics. Prentice-Hall, Inc., New York, New York. 1948. pp. 365-368.

3. Ruchhoft, C.C. The Possibilities of Disposal of Radioactive Wastes by Biological Treatment Methods. Sewage Works Journal, 21: 877-883 (September, 1949).

4. Anon. Calm Approach to Radioactive Waste Problems Urged. Chem. Eng. News, 27: 413 (February 14, 1949). Abstracted in Sewage Works Journal, 21: 603 (May, 1949).

5. Placak, O.R., and Lyle, K S. Unpublished information. ORNL reports in preparation.

6. Lauderdale, R.A., Jr. Unpublished information. ORNL reports in preparation.

7. Straub, Conrad P. Unpublished information. ORNL reports in preparation.

8. Ayres, J.A., McCullough, G.E., and Pitzer, E.C. Unpublished information.

9. Cook, G.B., and Wilkinson, J. Unpublished information.

Table 1

Some Long-Lived Products of High Yield[2]

Fission Product	Emission Yield	Half Life	Beta Energy-Mev	Gamma Energy-Mev
		Light Group		
$_{36}Kr^{85}$	0.24%	10 years	0.74	No
$_{38}Sr^{89}$	4.6	53 days	1.50	No
$_{38}Sr^{90}$	5	25 years	0.6	No
$_{39}Y^{91}$	5.9	57 days	1.53	No
$_{40}Zr^{95}$	6.4	65 days	0.39	0.73
$_{43}Tc^{99}$	6.2	9.4×10^5 years	0.3	....
$_{44}Ru^{103}$	3.7	42 years	0.2	0.56
$_{44}Ru^{106}$	0.5	1 year	0.03	See text.
		Heavy Group		
$_{52}Te^{129}$	0.19%	32 days	1.8	X-Ray, 0.3, 0.8
$_{53}I^{131}$	2.8	8 days	0.60	0.37
$_{54}Xe^{133}$	6	5.3 days	0.35	0.08, 0.03
$_{55}Cs^{137}$	6	33 years	0.5, 0.8	0.7
$_{56}Ba^{140}$	6.1	12.8 days	1.0, 0.4	0.5
$_{58}Ce^{141}$	6	29 days	0.55	0.21
$_{59}Pr^{143}$	6	14 days	1.0	No
$_{60}Nd^{147}$	2.6	11.0 days	0.4, 0.9	0.58
$_{61}Pm^{147}$	2.6	4 years	0.2	No

Table 2

Alum Coagulation Results

(After Placak and Lyle[5])

Element	Per Cent Removal	Remarks
I^{131}	Up to 10	Addition of small amounts of Cu, Ag, or C increased removals to 75 per cent.
P^{32}	98 plus	
Sr^{89}	10	Increasing turbidity from 50 to 1000 ppm increased removal efficiencies to 50 per cent.
Y^{91}	45 98	Using NaOH as alkali Using Na_2CO_3 as alkali Turbidity influencing factor too. For turbidity ranges of 50-1000 ppm removals ranged from 17 to 82 per cent.
Ce^{144}	98	Turbidity also influencing factor. For turbidity ranges of 50-1000 ppm removals ranged from 70-86 per cent.
Sr^{90} - Y^{90}	98 for Y 10 for Sr	On standing more of the Y daughter formed from Sr.

Essentially similar results obtained using iron as a coagulant.

Table 3

Phosphate Coagulation Results

(Lauderdale[6])

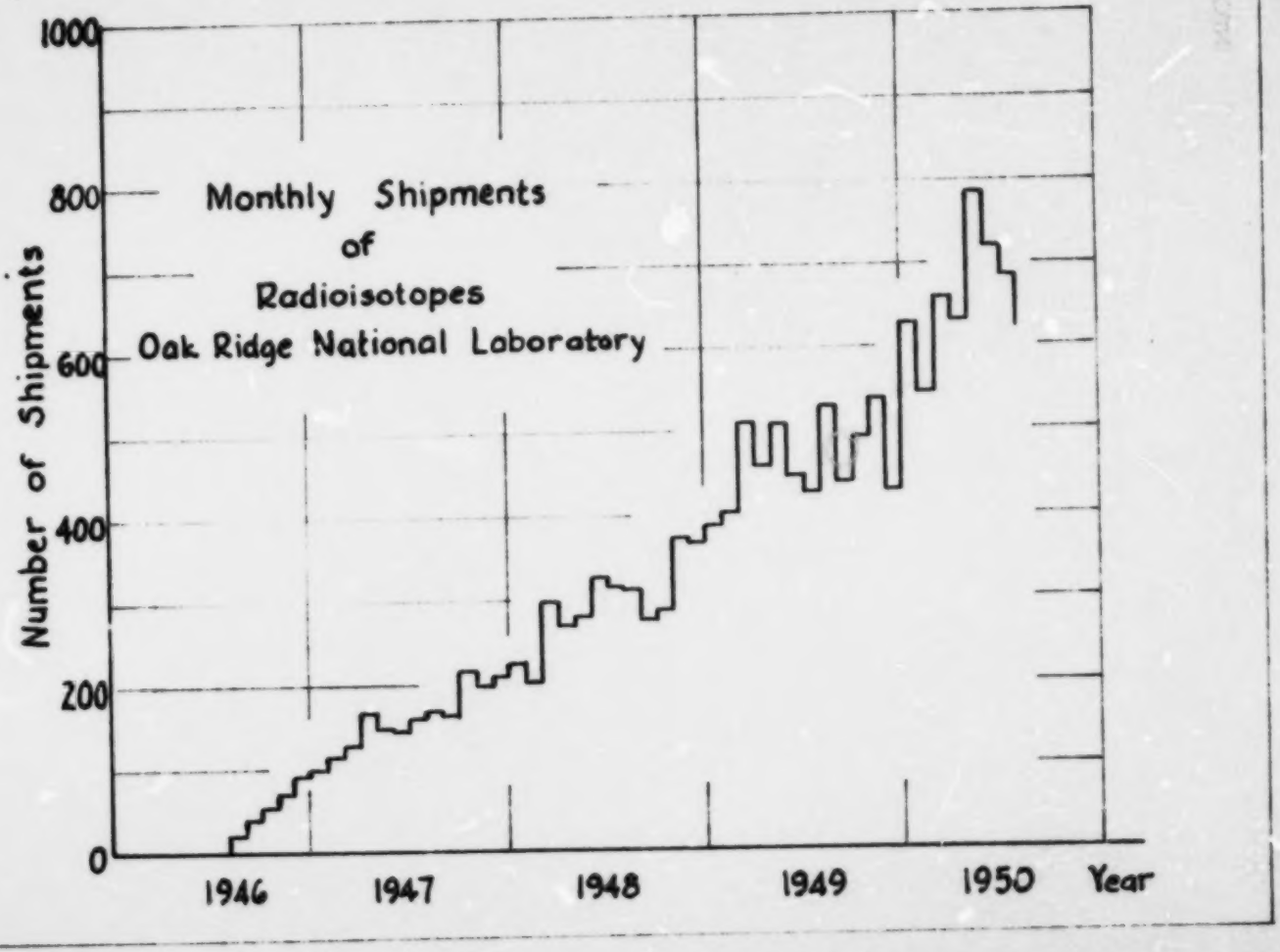
Element	Per Cent Removal
Zn^{65}	99 plus
Sr^{89}	98
Y^{91}	99 plus
Sb^{124}	67
Ce^{144}	99 plus
W^{185}	10

Table 4

Pilot Plant Results

(Straub[7])

Element	Treatment	Per Cent Removal
P^{32}	Coagulation with alum plus sedimentation	85
	Coagulation with alum plus sedimentation plus filtration	96-98
I^{131}	Coagulation with alum plus sedimentation (sodium silicate used too)	<1
	Coagulation, sedimentation plus filtration	<1
	Coagulation (alum, sodium silicate, alkali) plus carbon (5 ppm)	15
	Coagulation (alum, sodium silicate, alkali) plus carbon plus filtration	25


Monthly Shipments
of
Radioisotopes
Oak Ridge National Laboratory
Number of Shipments
1000
800
600
400
200
0
1946
1947
1948
1949
1950
Year